has probably been formed as an intermediate.[14] Because of the strain and steric protection of the cyclobutadiene ring by the isopropyl groups, the cyclobutadiene isomers shown above may be formed before insertion of a carbonyl group (to give tetraisopropylcyclopentadienone) or of another diisopropylacetylene moiety (to give hexaisopropylbenzene) can occur.

Acknowledgments.—We wish to express our gratitude to Mr. A. G. Sharkey, Jr., of the U. S. Bureau of Mines for determining mass spectral molecular weights and to Drs. Aksel Bothner-By, of Mellon Institute, and R. A. Friedel, of the U. S. Bureau of Mines, for discussion of the spectral evidence presented here. Mellon Institute provided facilities for the preparation of this manuscript.

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Gas Chromatographic Separation of the Hydrogen Isotopes[1]

Sir:

Considerable interest has been shown in the gas chromatographic separation of the six molecular species of hydrogen: H_2, HD, D_2, HT, DT, and T_2. The most recent work was summarized by Carter and Smith[2] and by King.[3] Since previous work was done at low levels of tritium, it was of interest to see whether comparable results could be obtained at higher tritium concentrations where radiation effects might impair separation factors. Glueckauf reported a decrease in the separation factor of radiokrypton and radioxenon with increasing radioactive power.[4]

Separation of the six hydrogen molecular species in a mixture that contained 2.4 c. of tritium is shown in Fig. 1. The column, ferric oxide coated alumina at 77°K., was similar to that described by Carter and Smith and by King. Separation factors calculated from this chromatogram and compared with those of Carter and Smith (~0.5 mc. of tritium) and King (~70 mc. of tritium) show no significant effect from the tritium radiation.

The separation factors in Table I were calculated in the manner described by Carter and Smith, *viz.*

$$\alpha_{1,2} = d_2/d_1$$

where d_2 and d_1 represent the distances from zero time to the peak maxima for respective components on the chromatograms. Direct comparison of separation factors defined in this manner is complicated by the decrease in retention times for peak maxima with increasing amounts of components, even for nonradioactive components. These decreases result from curvature of the sorption isotherms. The concentration dependence is particularly noticeable when comparing the separations of the five other species from H_2 in Table I. The higher separation factors reported by Carter and Smith are attributable to the shorter retention time for the H_2 peak as a consequence of increased

(1) The information contained in this paper was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) E. H. Carter and H. A. Smith, *J. Phys. Chem.*, **67**, 1512 (1963).

(3) J. King, *ibid.*, **67**, 1397 (1963).

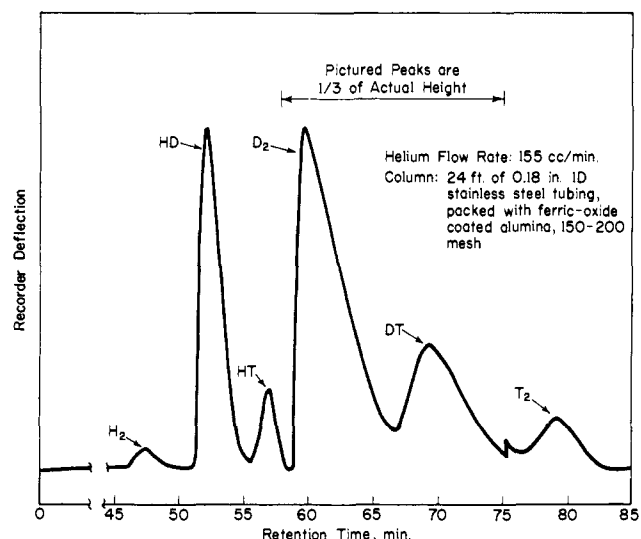(4) E. Glueckauf, *Ann. N. Y. Acad. Sci.*, **72**, 562 (1959).

Fig. 1.—Chromatogram of 5-cc. sample of hydrogen isotopes.

H_2 content of their sample (see Table II). When allowance is made for the effects of gross compositional differences, good agreement is observed between the separation factors derived by all three experimenters. In no case was there indication that the tritium radiation level had significantly affected the separation factor.

TABLE I

COMPARISON OF SEPARATION FACTORS FOR HYDROGEN SPECIES

α	This work	King[3]	Carter and Smith[2]
HD/H_2	1.09	1.13	1.22
HT/H_2	1.20	1.23	1.42
D_2/H_2	1.26	1.38	1.49
DT/H_2	1.45		1.85
T_2/H_2	1.66	1.68	2.08
HT/HD	1.10	1.09	1.22
D_2/HD	1.15	1.22	1.17
DT/HD	1.33		1.52
T_2/HD	1.52	1.48	1.71
D_2/HT	1.05	1.12	1.05
DT/HT	1.21		1.30
T_2/HT	1.38	1.30	1.47
DT/D_2	1.15		1.24
T_2/D_2	1.32	1.22	1.40
T_2/DT	1.14		1.13

TABLE II

COMPOSITION OF SAMPLES FOR HYDROGEN ISOTOPE SEPARATIONS

	Sample size, cc.[a]		
Component	This work	King[b]	Carter and Smith[b]
H_2	0.025	0.09	1.6
HD	0.48	0.08	0.7
HT	0.12	0.03	10^{-4}
D_2	2.8	0.08	1.0
DT	1.4	—	10^{-4}
T_2	0.16	0.01	10^{-5}
Total sample, cc.	4.985	0.29	3.3
Total activity, c.	2.4	0.07	0.0005

[a] At STP. [b] Concentrations estimated from information in ref. 2 and 3.

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1-Ethoxyphosphole 1-Oxide[1]

Sir:

We wish to report the synthesis of the very reactive heterocyclic phosphinic acid ester, 1-ethoxyphosphole 1-oxide (I).[2,3] The ester dimerizes too readily to allow its isolation, but it has been identified by its ultraviolet spectrum and by trapping it as a Diels–Alder adduct with cyclopentadiene. The synthesis from 1-ethoxy-2-phospholene 1-oxide[4] is given below.
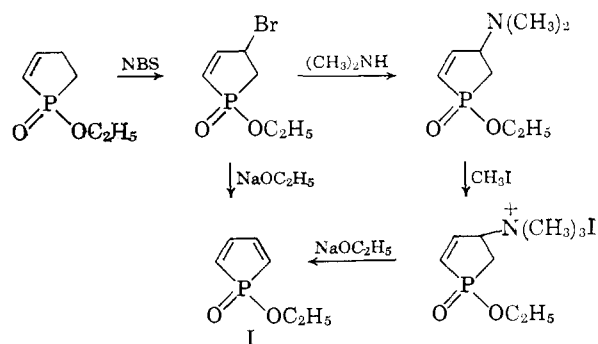
Both the bromide and the dimethylamino compounds are oils, and although the structures are reasonable on the basis of spectral evidence neither has been obtained pure. The quaternary ammonium iodide, crystallized from ethanol–acetone, melts sharply at 141–141.5°. *Anal.* Calcd. for $C_9H_{19}INO_2P$: C, 32.65; H, 5.78; I, 38.33; N, 4.23; P, 9.36. Found: C, 32.73; H, 5.87; I, 38.40; N, 4.27; P, 9.35. The iodide was converted in solution to the corresponding chloride by shaking in water with silver chloride; the resulting salt has an extinction coefficient of less than 2 above 240 mμ. When the quaternary ammonium salt in 0.0018–0.00046 M solution in ethanol is treated with sodium ethoxide (0.01 to 0.0017 M), it reacts at 25° to produce a compound to which the structure I has been assigned; λ_{max} 293 mμ (ϵ 1050); the rate constant for the elimination is roughly 10^2 1./mole sec. Compound I (identified by ultraviolet absorption and rate of dimerization) may also be prepared from the bromide, although here the approximate rate constant for its formation is only 3 1./mole sec. In ethanol, I undergoes a second-order reaction, with a rate constant at 25° of 0.55 1./mole sec., and concomitant disappearance of the absorption at 293 mμ. The rate of the dimerization is about the same in the presence of added potassium iodide, trimethylamine, acetic acid, or excess sodium ethoxide, although the reaction product decomposes in the presence of this last reagent. The phosphinate ester, I, is presumably saponified by aqueous alcoholic sodium hydroxide. The ultraviolet maximum of the product is shifted to 288 mμ, and the optical den-

(1) This research was supported by the National Science Foundation under Grant No. GP-2098.

(2) A number of substituted 1-phenylphospholes have previously been reported, but are relatively unreactive; F. C. Leavitt, T. A. Manuel, and F. Johnson, *J. Am. Chem. Soc.*, **81**, 3163 (1959); E. H. Braye and W. Hübel, *Chem. Ind.* (London), 1250 (1959); A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 2126 (1961); J. B. Hendrickson, R. E. Spenger, and J. J. Sims, *Tetrahedron Letters*, 477 (1961); I. G. M. Campbell, R. C. Cookson, and M. B. Hocking, *Chem. Ind.* (London), 359 (1962); G. S. Reddy and C. D. Weis, *J. Org. Chem.*, **28**, 1822 (1963).

(3) Preliminary reports describe three 1-phenylphosphole 1-oxides; see R. E. Donadio, *Dissertation Abstr.*, **20**, 495 (1959); E. Howard and R. E. Donadio, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 100P.

(4) U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron*, **19**, 1563 (1963).

sity decreases more slowly; apparently the anion dimerizes less readily than the ester. With a 50-fold or 100-fold excess of cyclopentadiene in ethanol at 25°, I reacts with a second-order rate constant of approximately 0.05 1./mole sec. to produce the Diels–Alder adduct, II. This compound has been purified by column chromatography over Woelm grade 1 alumina with elution by chloroform, followed by molecular distillation. *Anal.* Calcd. for $C_{11}H_{15}O_2P$: C, 62.84; H, 7.19; P, 14.74. Found: C, 62.50; H, 7.45; P, 14.48. Principal infrared absorptions occur at 3.22 (shoulder), 3.32, 6.32, 7.50, 8.22 (broad), 9.65 (broad), 10.52 (broad), 11.72, 11.99, and 13.21 (broad) μ. The complicated n.m.r. spectrum of II is consistent with the structure assigned, although the stereochemistry is uncertain.

II
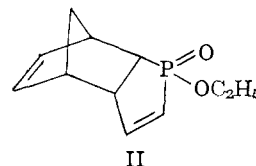
1-Ethoxyphosphole 1-oxide is similar in its absorption spectrum to thiophene dioxide,[5] (λ_{max} 289 mμ (ϵ 1230)), but is even more reactive than the latter. Research is continuing with the objective (among others) of preparing phosphinate esters with phosphorus at a bridge position of bicyclic systems.

(5) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

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Aliphatic Cyanates

Sir:

We wish to report the first synthesis of aliphatic cyanates.[1,1a]

Reasonably stable cyanates, R—O—C≡N, can be prepared if (1) the aliphatic group, R, is sufficiently bulky to prevent facile trimerization, and (2) the carbonium ion, R⁺, is of sufficiently high energy to minimize solvolysis (and rearrangement) of the cyanate under the conditions of synthesis.

Thus 1,4-dihydroxybicyclo[2.2.2]octane, 3-ethoxy-2,2,4,4-tetramethylcyclobutan-1-ol, or neopentyl alcohol, when treated successively with sodium hydride (or butyllithium) and cyanogen chloride, yielded the corresponding cyanates I (41%, m.p. 155–156°), II (30%, b.p. 63° (0.1 mm.)), and III (4.4%, b.p. 123° (185 mm.)).[2]
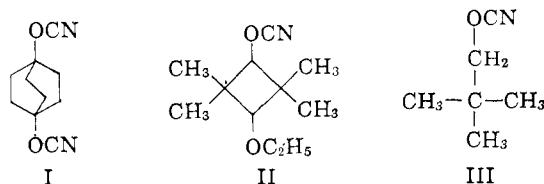
(1) The syntheses of several aromatic cyanates have recently been reported: (a) R. Stroh and H. Gerber, *Angew. Chem.*, **72**, 1000 (1960); (b) M. Hedayatullah and L. Denivelle, *Compt. rend.*, **256**, 4029 (1963); (c) D. Martin, *Angew. Chem., Intern. Ed. Engl.*, **3**, 311 (1964).

(1a) NOTE ADDED IN PROOF.—K. A. Jensen and A. Holm, *Acta Chem. Scand.*, **18**, 826 (1964), report the preparation of ethyl cyanate.

(2) Satisfactory elemental analyses and n.m.r. spectra for all new compounds were obtained.